

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/591,877
First Named Inventor : Max BRAUN
Filed : 10/10/2006
TC/A.U : 1621
Examiner : Jennifer Y. Cho

Docket No. : 14558-00001-US

Title : Production of compounds with CHF₂ or CF₂ groups.

DECLARATION UNDER 37 C.F.R. § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Dr. Max Braun, hereby declare as follows:

1. I am a citizen of Germany, residing at Varloh 8, D-30900 Wedemark (Germany).
2. I acquired a PhD in the chemical field at the University of Würzburg, Germany, and starting in December 1990, was employed at Solvay Fluor und Derivate GmbH, now Solvay Fluor GmbH, an affiliate of Solvay (Société Anonyme). In 2006, I was transferred to Solvay Organics GmbH, a German company and also an affiliate of Solvay (Société

Anonyme). I worked in both companies in the fields of synthesis and application of inorganic and organic fluorine compounds. I am the sole inventor and I am familiar with the invention described in pending claims as of the date of the declaration.

3. I am familiar with the cited prior art, namely the publication of O. Paleta, F. Liska and A. Posta in Collection Czechoslov. Chem. Comm., Vol. 35 (1970), pages 1302 to 1306, and US patent 6,509,495 B1 (G. Cordier et al.).

4. Paleta reports in said publication, among others, at page 1303 the preparation of the methyl ester of difluoroacetic acid by reaction between the methyl ester of difluorobromoacetic acid and zinc in methanol. Paleta substitutes hydrogen for a bromine atom. In my invention, I start with compounds having a $\text{CF}_n\text{XC(O)}$ group wherein n is 1 or 2 and X is chlorine, and I substitute hydrogen for a chlorine atom. Thus, Paleta breaks a carbon-bromine bond while my instantly claimed process requires breaking a carbon-chlorine bond.

5. It is well known in the art that carbon-bromine bonds have a lower bond energy than carbon-chlorine bonds. The bond energy of a carbon-bromine bond is 276 kJ/mol (= 66 kcal/mol) while the bond energy of a carbon-chlorine bond is 338 kJ/mol (= 81 Kcal/mol). This information can be found in the internet under the internet address <http://moon1.fccj.org/~ethall/2046/ch20/bondenergy/bondenergy.htm>. I attach a copy of the printed page in the annex.

6. The higher bond energy gives rise to the expectation that reaction of a C-Cl bond will, if ever it takes place, be more difficult than the reaction of a C-Br bond. Consequently, it was unpredictable whether a reaction of the type disclosed in Paleta would work with acceptable yield and selectivity when starting from chlorodifluoroacetic methyl ester.

7. To further illustrate the benefits of the instantly claimed invention I provide a further example which demonstrates the surprisingly high yield which can be obtained from chlorinated starting material.

14.4 g (100 mmol) of chlorodifluoro acetic acid methylester were refluxed with 13 g (200 mmol) of non-activated zinc dust in 50 ml methanol for 4 hours. According to a ^{19}F

NMR spectrum which was made from the reaction mixture the selectivity to difluoroacetic acid methylester was 81 %. The excess of zinc was removed by filtration, and the remaining solution was distilled under ambient pressure. The isolated yield of difluoroacetic acid methylester with a boiling point of 87 °C was 74 % of the theory.

8. The additional example shows a significant higher isolated yield than disclosed in Paleta, wherein the isolated yield value is approximately 50% at page 1303.

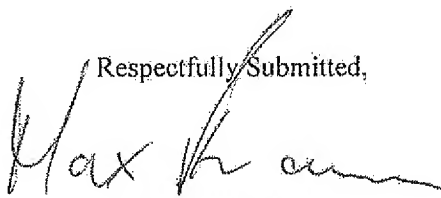
9. Obtaining a better result when carrying out a reaction of the type disclosed in Paleta with a chlorocompound instead of a bromocompound is an unexpected superior result in view of the difference in bond energies of carbon-bromine and carbon-chlorine bonds. Therefore, in the instantly claimed process, bromine and chlorine are not equivalent, but chlorine is unexpectedly superior to bromine.

10. All statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true, and further, these statements were made with the knowledge that willful statements and the like, so made, are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the patent application or any patent issued thereon.

Date:

27.08.2008

Respectfully Submitted,



Dr. Max Braun

Attachment

Printout of the internet page

"<http://moon1.fccj.org/~ethall/2046/ch20/bondenergy/bondenergy.htm> " as found on August 27, 2008

Bond Energies (page 900)

Enthalpies of formation (page 288) obtained experimentally.
However, Table 20.3 (page 901) and Table 20.4 (page 902) can be used
to estimate enthalpies of formation.

Table 20.3 Standard Heats of Formation (kJ/mol)

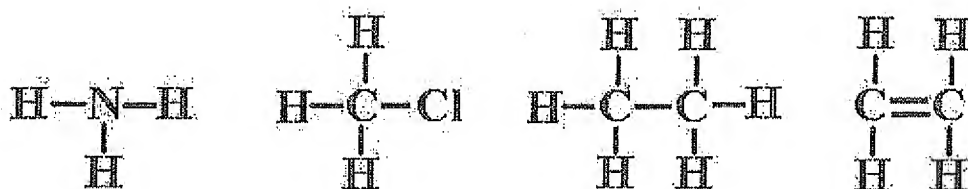
H	218	S	277
Li	162	F	79
Be	324	Si	450
B	560	P	332
C	717	Cl	121
N	473	Br	112
O	249	I	107

Table 20.4 Average Bond Energies (kJ/mol)

C-C	348	C-F	484	H-N	388
C=C	612	C-Cl	338	H-O	463
C≡C	960	C-Br	276	H-S	338
C-H	412	C-I	238	O-O	180
C-N	305	H-H	436	O=O	498
C=N	613	H-F	565	N-N	240
C≡N	890	H-Cl	431	N=N	612
C-O	360	H-Br	366	N≡N	945
C=O	743	H-I	299		

Examples:

Using Tables (20.3/20.4), estimate enthalpies of formation:



NH₃ (Table page 288 -46kJ)

$$\Delta H_{f(\text{N})} = 473 \text{ kJ} \quad \text{form 3 N-H bonds} \quad 3(-388 \text{ kJ}) = -1164 \text{ kJ}$$

$$\Delta H_{f(\text{H})} = 3(218 \text{ kJ}) + 1127 \text{ kJ}$$

$$\Delta H = +1127 \text{ kJ} - 1164 \text{ kJ} = -37 \text{ kJ}$$

CH₃Cl (Table page 288 -82kJ)

$$\Delta H_{f(\text{C})} = 717 \text{ kJ} \quad \text{form 3 C-H bonds} \quad 3(-412 \text{ kJ})$$

$$\Delta H_{f(\text{Cl})} = 121 \text{ kJ} \quad \text{form 1 C-Cl bond} \quad (-338 \text{ kJ})$$

$$\Delta H_{f(\text{H})} = 3(218 \text{ kJ}) - 1574 \text{ kJ} + 1492 \text{ kJ}$$

$$\Delta H = +1492 \text{ kJ} - 1574 \text{ kJ} = -82 \text{ kJ}$$

C₂H₆ (Table page 288 -85kJ)

$$\Delta H_{f(\text{C})} = 2(717 \text{ kJ}) \quad \text{form 6 C-H bonds} \quad 6(-412 \text{ kJ})$$

$$\Delta H_{f(\text{H})} = 6(218 \text{ kJ}) + 2742 \text{ kJ} \quad \text{form 1 C-C bond} \quad (-348 \text{ kJ}) - 2820 \text{ kJ}$$

$$\Delta H = +2742 \text{ kJ} - 2820 \text{ kJ} = -78 \text{ kJ}$$

C₂H₄ (Table page 288 +52kJ)

$$\Delta H_{f(C)} = 2(717\text{kJ}) \quad \text{form 4 C-H bonds } 4(-412 \text{ kJ})$$

$$\Delta H_{f(H)} = 4(218\text{kJ}) \quad \text{form 1 C=C bond } (-612 \text{ kJ})$$

$$+2305\text{kJ}$$

$$-2260\text{kJ}$$

$$\Delta H = +2305\text{kJ} - 2260\text{kJ} = +45\text{kJ}$$